THE EISENHOWER LIBRARY
3 1151 02563 4902
MORAVIA
SPEC. COLL.

54.375

Library

of the

Johns Hopkins University

Hedrick,
William Adam
1867
c.1

Paramido-orthosulfo-benzoic acid and some derivatives

Thesis for the Doctorate
Presented to
the faculty of Johns Hopkins University
by
William Adam Hedrick.

June 1887.

I here take the opportunity
to express my deepest gratitude to Professor
Remsen and Dr. Ira for the generous
advice they have taken to point out
the true path to success in chemical work, and
to Professor Remsen especially
for unfolding the marvelous charm of
research work to me
through the toils of my first effort.

Introduction 1

Historical

Limpricht & Uslar 1

Gmelin 2

Wurtz 3

Preparation of Ipsamide (O) sulphu

reous acid 10

Ethereous & Sulphu

reous Ethylsulphuric 17

Phenol 24

Salts of amido acid

Acid Barium Salt Preparation 13

Analysis 14

Analysis

Analysis of salts preparation

Preparation 15

Analysis 15

Äthan reihe 10

Substanzen Äthylalkohol 12

Propyl 16

Amylgruppe 18

Alkyl derivative 17

Methyl 24

Äthyl 27

Säure Amylalkohol

Butylalkohol 29

Propyl 30

Pentamethyl 30

Hexyl 30

Heptylcarbonsäure 30

Octyl 31

Nonylalkohol 31

Decyl 32

Undecyl 33

Introduction 1

Historical

Definition 3

Nomenclature 3

Classes 3

Preparation of Methyl derivatives

Methyl 4

Ethyl 4

Amyl 5

Ethyl 6

Preparation 6

Analysis 9

Properties of Formula of sulphur

Isomers 10

Diazo 10

Diazo Compound 12

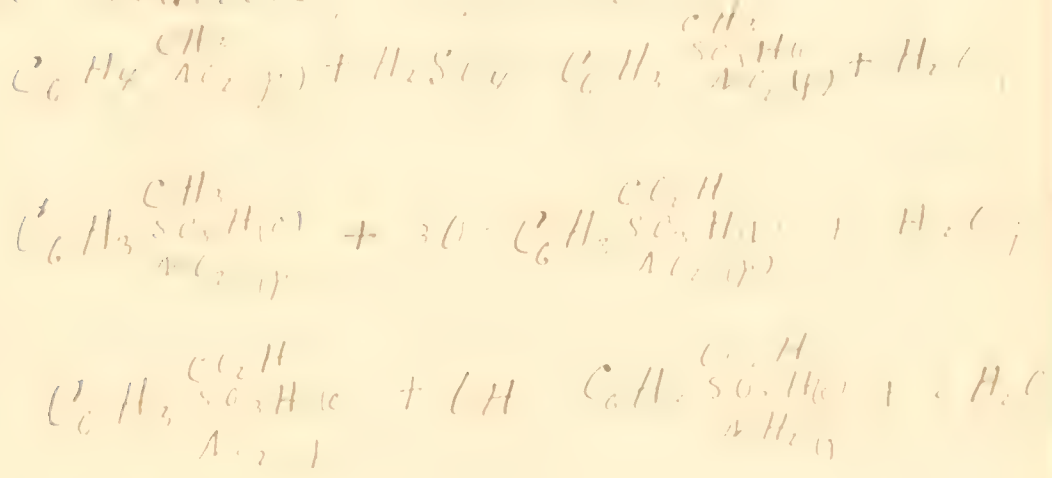
Preparation 12

Tables Work of 13

Analysis 21

Hydroxymail 64
Holmium
Calcium 81
Hardness 90
Boracic 92
Bo-th 94
Kölle 97
Kemzen 99
Yttrium 99
Deformation of 93
Salts of 96
Acid Basalt 96
Analysis 97
Basic Basalt 97
Analysis 97
Neutral Ca salt 98
Properties 99
Analysis 99
Crowning of crystal 100
Dimensions 102

Explanation of the Plates ... iv
Introduction ... 1
Description ... 21
Account of the Search ... 117
Bibliography ... 133



Ethyl-amido-amil

[illegible] was mixed with the molecular quantity of methyl iodide and [illegible] as soon as the alcohol was added [illegible] and the solution changed to a dark color. This was sealed and the tube left for three hours. The flask was opened and evaporated to dryness. The residue [illegible] ethyl iodide. This was treated with ether alcohol and the alcoholic extract evaporated to dryness. A small quantity of a resinous mass was obtained. The [illegible]

placed in a [illegible], in inverted condenser, with water, [illegible] and boiled for about two hours. This [illegible] in [illegible] a little water [illegible]
[illegible]
dryness. The residue [illegible] acid [illegible] and was boiled with barium carbonate. A soluble barium was first formed, but on continued boiling with barium carbonate an insoluble salt was formed. The acid or soluble [illegible]
[illegible]
by crystallization. The crystals resembled the original acid barium salt of the simple [illegible] acid. These crystals were analyzed and the analysis proved undoubtedly that no action had taken place.

[illegible] with [illegible] and [illegible]
[illegible] the oxide [illegible] dry, or, if the
[illegible] [illegible], [illegible]
decomposed.

Attempts to prepare the oxide.

Oxide [illegible] from the impure
[illegible] the oxide was found
in a flask with an equivalent quantity of
impure chloride and heated in an oil
bath to 140° for three hours. At no
time was there the evolution of a consid-
erable quantity of hydrochloric acid gas
nor was there a cool, dissolved in
dilute nitric acid. [illegible] and [illegible]
with the molybdenic test; neither a precipitate
[illegible] and was obtained
[illegible] solution. The [illegible]
in a flask and the [illegible]

the nature of the acid radicals in the more positive elements destroyed.

In the compounds of the acid radicals with positive elements, in the acid groups. If the two groups were both united to the acid group the basic property would be more weakened.

This might be tried by the action of hydrochloric acid on [illegible] and nitric and sulphuric acid obtained. This would decrease the basic and increase the acid properties of the compound. It would then act like an acid acid and not a basic.

by filtration, washed and dried by pressing between filter paper. The crystals were finally purified by recrystallization. The crystals do not readily dissolve, those of a dark color proved to not appear homogeneous. Three were analyzed.

			Calculated for
Salt taken	1.284	1.953	$C_6H_3 \overset{N(CH_3)_2}{SO_3 Ca}$
Weight $BaSO_4$	1.062	1.616	
Percent of Ca	14.34	14.38	14.13

The reaction may be represented by the following equation -

$$C_6H_3 \overset{NH_2}{SO_3 Na} + 2Cl + H_2O = C_6H_3 \overset{N(CH_3)_2}{SO_3 H} + 2NaCl.$$

Attempts were made to get the primary mass which was insoluble in water and soluble in alcohol to crystallize but it showed no signs of crystallizing

Ethyl amido acid

Ethyl amido phenyl succinic acid

[illegible] evaporating the water, under the [illegible] a gummy mass was obtained; [illegible] and filtered. On cooling a white crystalline substance was obtained. This was purified by crystallizing from hot water, in which it is easily soluble, while in cold water it is [illegible].

The new acid was analyzed

	Found	Calculated for $\left(C_6H_3\begin{matrix}CO_2H\\ CO_2HC_2H_5\end{matrix}\right)Ba$
Salt taken	.1430	
Weight of Ba SO_4	.0613	
Amount of Ba	21.42	21.52

The free acid is easily soluble in water, [illegible] soluble in alcohol, but not [illegible]

[illegible]

[illegible] [illegible] of [illegible] [illegible]

1. [illegible] [illegible] white lustrous needles, slightly soluble [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]. It is insoluble in alcohol and ether.

2. With potassium and sodium forms two kinds of salts, acid and neutral. The neutral barium salt is insoluble by which it may be distinguished from the other [illegible] benzoic acids.

3. [illegible] does not [illegible] [illegible] by [illegible] [illegible] [illegible]

with alkyl radicles, but forms
an alkyl amido-acid. It possesses
acid properties and forms salts.
The salts may be formed at the
nitrogen [illegible]

4. It does not unite
with acid radicles when in
the [illegible] of the free acid.

Discussion.

The simple [illegible]
have basic bodies [illegible] many amido-acids
their basic property when we [illegible]
expect it.

If a substituted acid
has its acid properties free or the
acidity unsaturated, it [illegible]

the acid like influence [illegible] many other radicals, which are in the [illegible] properties are neutralized by union with a base it no longer exerts so strong an influence and so allows the third radical to assume its own proper nature.

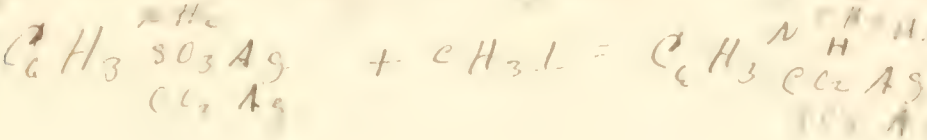
[illegible] many [illegible] exerts an influence over every other atom within the molecule.

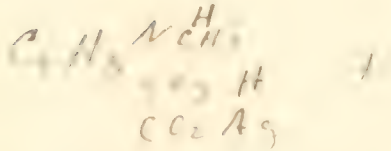
In the paraffin series the following method is a common one for the separation of amines; it is also a common method in order to substitute alkyl groups into the ammonia residue of aniline and certain of its derivatives viz; to treat ammonia or substituted

anilin with alkyl halogens.

Salts are then formed similar to ammonium and the free bases obtained by treating the salt with alkali

takes place in the present case only the metal in the salt plays the part of the free alkali. It may be represented by the following equation:





And this taking place again would yield the product .

The second case where the metal barium salt of monethyl amido was

Ethionol can only be explained by assuming that the methyl compound is first formed and that this subsequently reacts with alcohol forming ether and the corresponding mercaptan according to the equation

$$C_6H_3\begin{cases}N\begin{cases}C_2H_5\\C_2H_5\end{cases}\\SO_3H\\SC_2H\end{cases} + C_2H_5\text{-}OH = C_6H_3\begin{matrix}\overset{C_2H_5}{\hat{H}}\\C_2H\\SO_3H\end{matrix}$$

$+ (C_2H_5\text{-})_2O$;

or the entire reaction may be expressed thus

$$C_6H_3\begin{cases}NH_2\\CH_3\\SO_3H\end{cases} + 2\,C_2H_5\text{-}I + C_2H_5OH =$$

$$C_6H_3\begin{cases}NC_2H_5\\CH_3\\SO_3H\end{cases} + 2\,HI + (C_2H_5)_2O.$$

This is in accordance with the explanation given by Remsen & Palmer[12].

Hallock[25] found that with the
chloride of benzoyl-toluene-sulfonamide
the original acid was obtained
and not the ethereal salt.

Benzoic acid

Benzoic acid is produced
by Fownes + Palmer[26] but they did not
give any mode of preparation

Preparation of benzoic acid

The amide used, without purification,
was suspended in water & heated to
incipient redness with an excess of

to metals than on nitrogen the latter being
one of the metals was examined.

I was hoped that amines
could be obtained and the

The ammonium salt was
made by adding just sufficient ammonia
to dissolve the cupric salt. Both
large quantities of ammonia the salt
used was conducted into the solution.
about one half hour or less a crystalline
compound was deposited. The mass
filtered washed and dried.

On heating with caustic
alkali no odor of ammonia was
perceptible. Subsequent experiments
have shown that it was not chemically

the neat barium salt was [illegible]
decolorized in a large quantity [illegible]
and nitrous acid conducted into the
[illegible]. The solution [illegible] metaboric
acid much [illegible]
a white crystalline [illegible] was [illegible]
the dry [illegible] compound made in the other
way. The solution was filtered, and
dried. On cooling [illegible] the filtrate was
in the shape of small [illegible] [illegible]
by melting without [illegible] and
[illegible] barium, [illegible]
barium nitrate, $Ba(NO_3)_2$, [illegible]
[illegible] compound
the anhydrous salt was used [illegible]
[illegible] determined
salt by [illegible] which was made
in an atmosphere of [illegible]

and weighed the gas over mercury
[illegible]

Analysis of Hydrocarbon

Wt taken	.0999 gm	.5763 gm
Volume of N	74.32 cc	64.45 cc.
Temp	17.5	20.
Barometer	764.5 mm	758.8 mm
Wt. Weight of CO2	.0861	.497 gm.
Percentage C	12.31	12.24

Analysis from combustion

Wt taken	[illegible]
Vol N	4811 cc
Temp	20.
Bar	758.7
Weight of N	.0351
Percentage C	[illegible]

Calculated for C_6H_{12}

Antimonic acid.

[illegible] was by Fremy. This was studied more particularly by Rammelsberg. It was obtained by treating [illegible] with nitric acid. [illegible] work. The acid is soluble in alcohol, water, and ether. It readily absorbs [illegible] from the air. [illegible] were made, with acid, neutral and [illegible] K, Na, Ca, Ba, Zn, Pb and Ag [illegible]

were the last stated in table.

Benzoate of lead melting at
with water forked out, obtained
in eight acid and found

Boric obtained on
treating acid by sulphuric
acid with sulphur dioxide. Was
also quantity studied in Sodium.

The acid was obtained from the lead salt.
Crystallized in greenish needles,
soluble in ether, soluble in alcohol
and water. Neutral and basic
salts of Pb & Pb(OH)₂. The basic lead salt
were prepared

with cooled forked quick potassium
acid. It is therefore dibasic tetra
basic acid.

K. Kraut[1] obtained methyl (Phenyl)
sulphone acid by heating (Phenyl) sulphonic
acid with sulphuric acid. The acid
crystallizes in white needles soluble
in alcohol, insoluble in ether.
The K, Ba, Ca, Pb and Ag
salts were prepared and analyzed.

Kraut[2] also worked upon
the acid especially in regard to the
formation of protocatechuic acid from
sulphoxybenzoic acids.

Spiess[3] obtained from a hydroxy-sulpho-benzoic acid by
heating with sulphuric acid. It forms white
flakes and can be crystallized from water
or ether, soluble in alcohol, the
crystals soluble in water and alcohol.

The acid was obtained in crystals by decomposing the lead compound obtained from the ammonium salt. The ammoniacal liquid was neutralized with nitric acid, placed under a bell jar over sulphuric acid and allowed to evaporate spontaneously. Crystals were obtained. These on exposure to the air deliquesced. The sulphur acid gave a slight red color to ferric chloride. Neither the aqueous solution of the acid alcohol nor ether were added but in neither case was any thing precipitated. The reaction may be expressed thus:

$$C_6H_5\left\{\begin{matrix}SO_3H\\C_2H\end{matrix}\right. + HCl \quad C_6H_5\left\{\begin{matrix}SO_3H\\C_2H\end{matrix}\right. + Pt\ldots$$

Preparation of salts.

The colour of the acid solution was partially destroyed by boiling with animal charcoal.

Barium salt.

The acid solution was boiled with barium carbonate. A white salt was formed at first, but by continued heating with barium carbonate an insoluble salt was formed. The barium salt is insoluble in water [illegible] acetic acid but soluble in dilute hydrochloric acid. The soluble barium salt on the evaporation of solution would not crystallize but separated as a powder. When obtained in aqueous

[illegible] the salt crystallized out in
[illegible] the residue was filtered
[illegible] and evaporated to dryness. Weighed
[illegible] gave [illegible].

Analysis of salt dried at 110°.

	Found	Calculated for $(C_6H_{11}O_6)_2Ba$
Ba SO_4	.0944 .0753	
Found Ba	22.02 23.76	23.79

The neutral [illegible] was also made by neutralizing with ammonia solution and evaporating to dryness. The [illegible] was also analyzed.

	Calculated for $(C_6H_{11}O_6)_2Ba$
Salt taken .6220 .4995	
Weight Ba SO_4 .3178 .2552	
[illegible]	[illegible]

[illegible] Station [illegible]

We used caustic on [illegible]
Solution caused the caustic [illegible]
was allowed to crystallize. Beautiful
crystalline columns, resulting in
[illegible]
These were as much as [illegible]
to thirty millimeters in length
and of sufficient size to measure.
Mr. Gill a student in
Mineralogy, has kindly measured and
drawn the crystal for me. There
is probably another salt formed in
the reaction but on allowing the caustic
to stand a granular precipitate
[illegible]
was separated and measured.
I am very anxious to get the crystals

Crystal [illegible] salt.

The [illegible] [illegible] [illegible] elongated in the direction of vertical axis.

[illegible] [illegible] [illegible] [illegible] [illegible] obtained by taking the mean of [illegible] [illegible] [illegible] are as follows, viz; [illegible] 129° 11'

[illegible] 134° [illegible]

[illegible]

[illegible]

[illegible]

Though the amplitude was quite
small the arc described must
be considered. The rounding of the
[illegible] has caused a large variation in the amount
but the more perfect ones give very
[illegible]

A. C. Gill.

acid

Hydrazine [illegible].

This important group of nitrogen compounds has not been studied in an exhaustive manner. The most important work upon the subject was by E. Fischer. Since that time they have been studied by a number of chemists.

Of the different methods for preparing these bodies I have used the reduction of their corresponding diazo salts.

Reduction.

The diazo compound as previously described was added to a cold saturated solution of sodium [illegible]. [illegible]

and the solution allowed to cool and [illegible]. [illegible] [illegible] when treated with sulphuric acid but they were so mixed with other substances that no definite statement could be made. [illegible] fluorescence in alkaline solution.

Haller[23] in order to obtain the hydrocarbon from pseudocumyl hydrazine boiled it with dilute (ten percent solution) of solution of copper sulphate.

In addition to the properties given above the hydrazine [illegible] with barium carbonate gives a precipitate; the solution was given

Review -

I have obtained several salts of the original amide acid and the calcium and barium salt of the ethyl derivative of the same; the diazo derivative and from this the corresponding oxy acid and a basic barium and neutral calcium salt; the corresponding hydrazine compound and probably the ortho-

Bibliography

1 Campbell & Adam Ann. 16 47
2 Green J. Ch (2) 3 241
3 Hunt Ann. Ch. Vol 1 340
4 Borges Ann. 202 65
214 347
5 Green Ber. 5 16 35
6 Hahnemann Chronische Krankheiten 1832
7 Richter Ber. 9 401
8 Gradmann " 9 1913
9 Ellmann " 17 2719
10 Klemann " 19 336
11 Piccini Ann 92 326
12 Simon & Palmer Ann Ch J Vol 8 233
13 Zander Ann 198 1
14 Cahours Ann Chim Phys (3) 13 92
15 Mendius Ann 163 39
16 Kekulé " 179 167
17 Barth " 143 35

18	[illegible]	Jan 1[illegible]	[illegible]
19	Köhler	" 1644	130
20	Kramer	Juli 1871	294
21	Kriese	Jahr. Ber. 1864	340
22	E. Fischer	Jan 190	67
23	Gerhardt	" 108	214
24	Walker	Ber. 5	137
25	Wallach	Ann. 214	193
26	Kremers & Palmer	Am Ch. J. Vol 8	151

Benzoylbenzosulphamid.

The present investigation was undertaken in order to determine whether, when benzoyl chloride acts upon benzosulphamide, it simply replaces a hydrogen atom of the amido group, or whether it acts as a dehydrating agent, and finds the water [illegible] needed upon the new chloride.

These two views may be represented by the two following formulae:

1 $C_6H_5SO_2.NH_2 + C_6H_5COCl =$

$C_6H_5.SO_2.NH + HCl$

$C_6H_5.CO$

2 $C_6H_5.SO_2.NH_2 + (C_6H_5CO)Cl =$

$C_6H_5.SO_2.NCO + H_2O$

C_6H_5

The latter reaction will be used to
obtain the former by the reaction

The reaction used was suggested
by Ramsay & Palmer[1] viz; a comparison of
the ethereal salts obtained from the
acid by heating with phosphorus
pentachloride and alcohol; and by
heating the metallic salt with alkyl
iodides.

Spiridonoff[2] Volkow[3] and
Wallach[4] have shown that, when benzene-
sulphonic acid is treated with phosphorus
pentachloride, the chloride of sulphonyl
is converted into the sulphinyl chloride

by treatment with alcohol or water.

Preparation of tolylene-sulphonic

[illegible] by the method originally employed by Stenhouse[1] and slightly modified by [illegible] and Tollens.[2]

I found that it was best to use a sand-bath and raise the temperature to not to 185°. Both of the sulphonic acids of the benzene and the [illegible] and the [illegible].

The one converted into the sulphon-chloride by treatment with phosphorus pentachloride and then into amide by shaking it strongly with ammonia

a modification which can be
better method for preparing the cyanide from the
chloride the following experiment was made.
Twenty grams of potassium sulphocyanate
was placed in a long mortar and the calculated
quantity of phosphorus pentachloride added
to mixture was continually stirred and
rubbed with a pestle. When the reaction
had ceased the product was powdered and
carbonate. By the former 10 grams by
the latter 7 grams of sulphocyanide was obtained
the theoretical is sixteen grams. The
decomposition with dilute sulphuric acid
to be preferred.

The benzoyl compound was then
made from thiocyanic acid by Herbst's
flask containing the benzoyl-
sulphocyanide and benzoyl chloride was arranged
provided was heated for three hours

[illegible] was [illegible]
[illegible] [illegible] to about 110°. When
cool it was decanted in dilute acetic
[illegible] and
in the form of a crystalline powder
[illegible]. The melting point was
144.5° 147 uncorrected. From this
the neutral ammonium salt was made,
and by adding nitrate of silver the
silver salt was precipitated as a white
mass.

The silver salt and the calculated
molecular quantity of ethyl iodide
[illegible] were
sealed in a water-bath for a little over
two hours. Action took place shortly
after heating and was shown by a
change of color. The mass was
extracted with alcohol and upon cooling
the crystals would crystallize out

acid and an equal bulk of water
shaken with ether, found 14.6 14.7°.

The lead salt acted in a
similar manner.

From the lead salt the potassium
salt was obtained by precipitating the
lead with potassium sulphate, filtering,
evaporating to dryness and redissolving
the potassium salt in alcohol.

This with the necessary
quantity of ethyl iodide was put into
a pressure flask and placed in boiling
water. After about an hour the flask was
opened and the alcohol evaporated. The
mass was boiled with water to remove
potassium iodide. The insoluble in the
flask in small quantity, gave oil which
solidified on standing and a white
crystalline body. Both of these
dissolved in alcohol. The oil separated

Bibliography